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Intermediates and Transition Structures of the Benzannulation of Heteroatom-Stabilized Chromium Carbene Complexes with Ethyne: A Density Functional Study

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Abstract: We present a density functional study of the benzannulation reaction of heteroatom-stabilized chromium pentacarbonyl carbene complexes with ethyne. According to our calculations, the benzannulation is, independent of the detailed mechanism, exothermic both for hydroxy- and amino-substituted phenyl- and vinylcarbene compounds. The benzannulation starts with a dissociation of the *cis*-CO molecule closest to the π-system within the carbene ligand and a subsequent ethyne coordination, producing highly energetic η^2-ethyne−carbene complex intermediates. The following ethyne−carbene coupling, leading to η^3-allylidene complex intermediates, explains the observed regioselectivity of the benzannulation. The next step is a CO insertion. In the case of phenylcarbene educts, η^4-vinylketene complex intermediates are formed, which react to η^4-cyclohexadienone complexes by ring closure, whereas in reactions of vinylcarbene educts, the CO insertion produces η^4-cyclohexadienone complexes without any further barrier of activation. η^4-Vinylketene complexes are the most stable, but only weakly exothermic, intermediates along the naphthol formation and η^4-cyclohexadienone complexes are the most stable and strongly exothermic intermediates in the phenol formation. This has remarkable experimental consequences: formation of six-membered rings should rarely be observed for *ortho*-disubstituted phenylcarbene chromium educts, whereas vinylcarbene compounds should generally produce six-membered rings. All reaction steps except the rate-determining *cis*-CO dissociation are characterized throughout by a pronounced template character and low-energy barriers. We find that the exchange of a *cis*-CO with a σ-electron-donating solvent molecule is significantly less endothermic for metal hydroxycarbene than for aminocarbene. This explains the experimentally observed higher reaction temperature needed for the reaction of aminocarbene compared to hydroxycarbene compounds. Only in the case of tetracarbonyl vinylcarbene complexes is an intramolecular saturation of the vacant ligand site, forming η^3-allylidene complexes, an alternative to an intermediate coordination of a solvent molecule.

Introduction

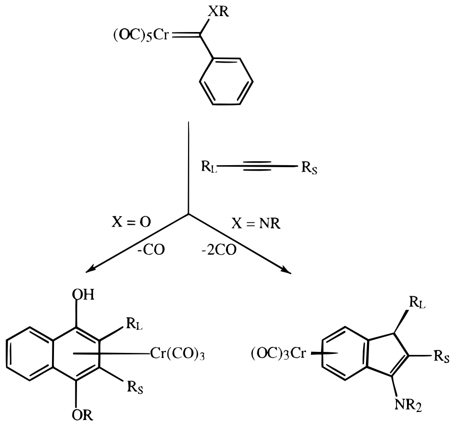

Figure 1. Cycloadditions of heteroatom-stabilized chromium carbene complexes with alkynes−heteroatom effect.

During the past 2 decades, transition metal−carbene complexes have developed from exotic organometallics to useful reagents for the selective formation of carbon−carbon bonds. Whereas Schrock-type compounds[1] have turned out to be efficient catalysts for olefin metathesis, Fischer metal carbenes,[2] $(OC)_5M{=}C(R)R^1$, are mostly employed in stoichiometric reactions. Among the Fischer compounds, heteroatom-stabilized chromium carbene complexes containing a π-system next to the carbene carbon atom have been found to be of particular synthetical value.[3−7] They allow novel types of cyclization reactions in which the $Cr(CO)_3$ group acts as a template center for the annulation of the carbene ligand by an alkyne. In the case that also a carbon monoxide ligand is incorporated into the final product, aromatic six-membered rings can be found, a reaction known as transition-metal-induced benzannulation,[8] which corresponds formally to a [3 + 2 + 1] cycloaddition. In other cases it is found that insertion of a CO does not take place, and five-membered rings are obtained. If an aminocarbene ligand is utilized instead of an alkoxycarbene ligand, cyclopentannulation prevails in most cases over benzannulation (Figure 1). This is referred to as the heteroatom effect, generally believed to be attributable to the better donor capacity of

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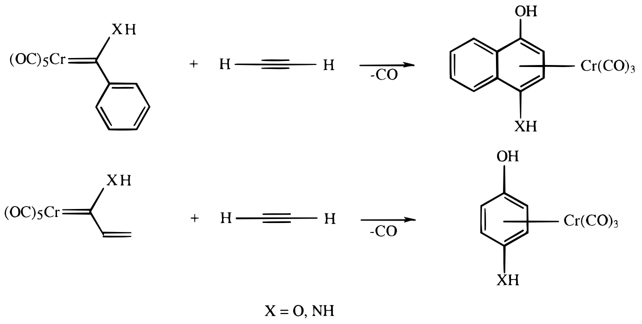

Figure 2.

nitrogen over oxygen. This is in agreement with the observation that N-acylation favors the formation of benzannulation products.[9] Only very recently, successful benzannulations were reported for pyrrolocarbene,[10] amino-stabilized alkenyl carbene,[11] and aminocarbene complexes at which the alkynyl group is connected to the amino group via a C$_2$-arene bridge,[12] producing aminonaphthol, aminophenol, and indene derivates, respectively. For synthetic use, it is decisive that the benzannulation proceeds regioselective. The sterically more demanding alkyne substituent is directed next to the OH group in the final hydroquinone product.

Because of its applicability to a broad spectrum of substituents, its regioselectivity, and its mild experimental conditions, benzannulation has been employed as key step in the synthesis of a series of natural compounds.[13,14] Since in contrast to its synthetic applications the theoretical knowledge of such kind of metal-induced cycloaddition reactions is rather limited (see ref 15−17 for proposed mechanisms), we studied mechanistic and energetic aspects of the following reactions at the density functional theory (DFT) level[18,19] (Figure 2).

Early studies have shown that reactions of chromium carbene complexes with alkynes will be suppressed in the presence of external CO.[20] This makes it most probable that a carbon monoxide ligand will dissociate at the first step, which has later been verified by kinetic studies.[21] The subsequent alkyne coordination to the metal center is believed to form an η^2-alkyne−carbene complex intermediate. Calculations at the extended Hückel level[22,23] predict only small metal−alkyne interactions. If the alkyne−carbene coupling is blocked by employing an *o*-alkynylaryl−carbene complex—which connects the alkyne and carbene groups through a rigid C$_2$ arene group—an η^2-alkyne−carbene complex can be stabilized[24,25] (see Figure 10). X-ray analyses and ^{13}C NMR studies also indicate a loose η^2-coordination of the alkyne to the metal.

The following steps of the annulations proceed so fast that kinetic measurements are not feasible. A planar chromacyclobutene was suggested as initial product of the alkyne−carbene coupling step,[26] but extended Hückel calculations by Hofmann *et al*.[22,23] indicate that planar chromacyclobutenes have to be characterized as coordinatively unsaturated 16-electron open-shell species with high energy. Instead, η^3-vinylcarbene/η^3-allylidene complexes were found to be stable 18-electron valence isomers and should therefore be considered as more reasonable intermediates. Recently, this kind of complex was experimentally isolated and characterized by X-ray as product of a reversible CO dissociation from a chromium pentacarbonyl aminovinylcarbene complex,[27] as well as isolated and characterized by ^{1}H and ^{13}C NMR as subsequent alkyne insertion product.[27]

A carbon monoxide insertion leading to η^4-vinylketenes **4** (Figure 3) as intermediates is generally believed to be the next reaction step. Although experimental evidence has been provided for the formation of such complexes, no such complex has ever been observed during a benzannulation reaction itself. So far, two η^4-vinylketene complexes of chromium have been isolated and structurally characterized as enaminoketene complexes,[28,29] along intramolecular alkyne insertions into aminocarbene complexes. These insertion reactions lead to a variety of carbon monoxide-containing products.[28−30]

Recently, a nontautomerized η^4-cyclohexadienone molybdenum complex was isolated in which the final tautomerization to the phenol product had not occurred.[31]

Finally, attention has already been focused on the reactive behavior of substituted aryl(alkoxy)carbene chromium complexes[32] and alkenyl(alkoxy)carbene complexes,[14,33] respectively. 2,6-Disubstituted aryl complexes **9** have never been observed to give hydroxyarenes **10** or η^4-benzocyclohexadienones upon reactions with alkynes but rather lead to indenes **8** (Figure 4). In this case, cyclopentannulation occurs without insertion of a carbon monoxide ligand.[32] However, it has been shown that cyclization reactions of *ortho*-disubstituted arylcarbene tungsten intermediates—generated by protonation of the tungsten carbyne precursor—with $MeC\equiv CMe$ lead to the formation of η^4-cyclohexadienones **A** (Figure 5).[34]

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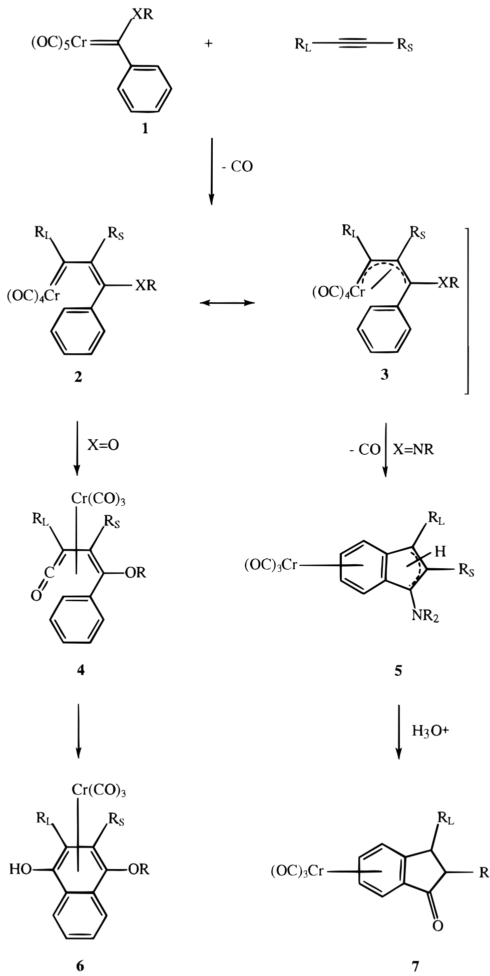

Figure 3. A simplified representation of the general mechanistic proposals.

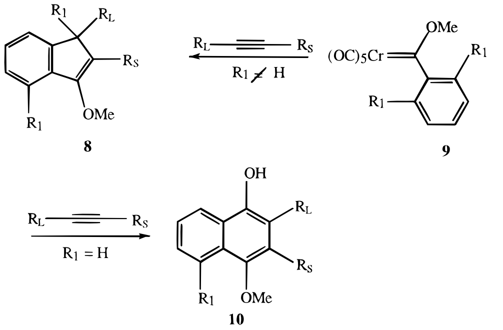

Figure 4. Reactions of unsubstituted/substituted phenylmethoxycarbene chromium complexes, summarized according to ref 51.

Alkenyl(alkoxy)carbene complexes **11**, on the other hand, are usually found to insert a carbon monoxide ligand upon reaction with alkynes, giving either cyclohexadienones **12**[33] or phenols **13**[14] as products (Figure 6).

Methods of Computation

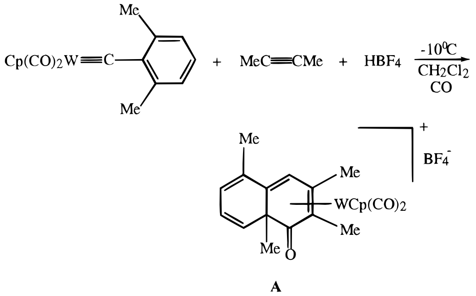

Figure 5. Annulation reaction of a protonated *ortho*-disubstituted phenylcarbyne tungsten complex according to ref 34.

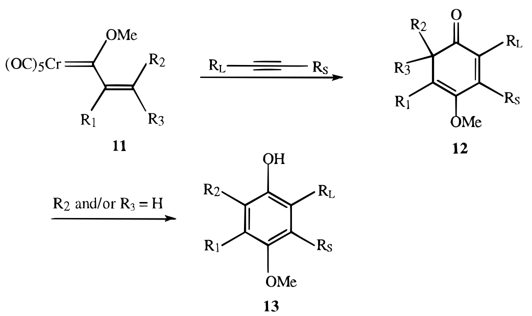

Figure 6. Reactions of unsubstituted/substituted vinylmethoxycarbene complexes, summarized according to ref 51.

DFT[18,19] geometry optimizations have been performed with a DFT version[35] of the program system TURBOMOLE.[36] The Vosko−Wilk−Nusair density functional[37] with Becke's exchange[38] and Perdew's correlation[39] (BP86) corrections has been employed. We used gridsize 1 for energy calculations and gridsize 3 for gradient calculations, as recommended.[35] The eigenvector following[40] algorithm, adapted from the program system MOPAC[41] for our purposes, has been used throughout all geometry optimizations and saddle point searches. No symmetry constraints have been imposed in any optimizations. Only closed-shell states were considered.

We investigated the reaction mechanisms by working with internal coordinates. Geometric dummy atoms were included to define stable coordinates and to perform the geometry optimizations efficiently. Of the $3n - 6$ (n =number of real atoms) internal degrees of freedom of our systems, we kept $3n - 7$ free and employed the remaining internal coordinate as "reaction coordinate", *i.e.*, we gradient-optimized the structure for fixed values of this coordinate, varying the latter in a stepwise fashion. The stepsizes varied from 50 to 0.5 pm in the region of an expected transition structure. All transition structures presented here were obtained by this method, and their nature has been checked by calculating the cartesian Hessian numerically.

We used split valence (SV) basis sets[42] on all atoms: (14s8p5d)/[5s2p2d] on chromium; (7s4p)/ [3s2p] on carbon, nitrogen, and oxygen; and (4s)/[2s] on hydrogen. The minima and transition structures were reoptimized by employing SVP basis sets.[42] In this case, the additional polarization functions were 1p (0.120675) for chromium; 1d for carbon (0.8), nitrogen (1.0), and oxygen (1.2); and 1p (0.8) for hydrogen. From our results it is apparent that in the case of weak multihapto (η) Cr−C interactions and for a realistic description of the—for our purposes much less important—C−O distances, the SV basis set has to be augmented by polarization functions. All given energies, bond distances, etc. refer to results obtained with the BP86 density functional and the SVP basis set. Selected results obtained with the SV basis set are available as supporting information.

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Table 1. Calculated and Experimental Cr−C, C−C, and C−O Bond Lengths (pm) of Heteroatom-Stabilized Chromium Carbene Complexes

compound	bond	length (pm)	bond	length (pm)
$Cr(CO)_6$	Cr−C	190	C-O	116
		191[a]		115[a]
expl[b]		191		114
$(OC)_5Cr{=}C(OH)(CH{=}CH_2)$	$Cr{-}C_{carbene}$	203	$C_{carbene}{-}C_{vinyl}$	147
$(OC)_5Cr{=}C(OH)(C_6H_5)$	$Cr{-}C_{carbene}$	205	$C_{carbene}{-}C_{phenyl}$	148
expl[c]		204		147
$(OC)_5Cr{=}C(NH_2)(CH{=}CH_2)$	$Cr{-}C_{carbene}$	208	$C_{carbene}{-}C_{vinyl}$	148
$(OC)_5Cr{=}C(NH_2)(C_6H_5)$	$Cr{-}C_{carbene}$	207	$C_{carbene}{-}C_{phenyl}$	149
$(OC)_5Cr{=}C(OH)(CH{=}CH_2)$	$Cr{-}C_{trans}$	189	$C_{trans}{-}O_{trans}$	116
$(OC)_5Cr{=}C(OH)(C_6H_5)$	$Cr{-}C_{trans}$	189	$C_{trans}{-}O_{trans}$	116
expl[c]		187		113
$(OC)_5Cr{=}C(NH_2)(CH{=}CH_2)$	$Cr{-}C_{trans}$	188	$C_{trans}{-}O_{trans}$	116
$(OC)_5Cr{=}C(NH_2)(C_6H_5)$	$Cr{-}C_{trans}$	188	$C_{trans}{-}O_{trans}$	116
$(OC)_5Cr{=}C(OH)(CH{=}CH_2)$	$Cr{-}C_{cis}$[d]	189	$C_{cis}{-}O_{cis}$[d]	116
$(OC)_5Cr{=}C(OH)(C_6H_5)$	$Cr{-}C_{cis}$[d]	189	$C_{cis}{-}O_{cis}$[d]	116
expl[c]		189		116
$(OC)_5Cr{=}C(NH_2)(CH{=}CH_2)$	$Cr{-}C_{cis}$[d]	189	$C_{cis}{-}O_{cis}$[d]	116
$(OC)_5Cr{=}C(NH_2)(C_6H_5)$	$Cr{-}C_{cis}$[d]	189	$C_{cis}{-}O_{cis}$[d]	116

[a] Ziegler's nonrelativistic value from ref 49. [b] References 52 and 53. [c] Data from the crystal structure of (phenylmethoxycarbene)pentacarbonylchromium from ref 48. [d] CO ligand which is next in space to the π-system within the carbene ligand.

We additionally checked the important energy barriers by performing single-point calculations with the "Becke-3-LYP" (B3LYP) hybrid functional[43] as implemented in the GAUSSIAN 94/DFT program system,[44] using the SVP basis sets. The B3LYP hybrid functional employs the exchange energy and correlation energy from the local density approximation,[37] Becke's exchange correction,[38] the Hartree−Fock exchange, and the correlation functional developed by Lee, Yang, and Parr.[45]

Kinematical relativistic effects are unimportant for an accurate calculation of chromium complexes and have been neglected in our calculations.

Structure of Heteroatom-Stabilized Chromium Pentacarbonyl Carbene Complexes

Various configurational and conformational arrangements are possible for heteroatom-stabilized pentacarbonyl chromium carbene complexes containing a π-system next to the carbene carbon atom, due to rotations about (*i*) the bond connecting the carbene carbon atom and the α-carbon atom, (*ii*) the carbene carbon−heteroatom, and (*iii*) the chromium−carbene bond. Among these configurations, those with the α,β-double bond and the chromium atom on the same side of the bond connecting the carbene carbon atom and the α-carbon atom (forming a cisoid system of two formal double bonds) are most sensible as starting geometries for the benzannulation. These orientations are generally observed for solid state structures (Schubert in ref 4). Within this configurational constraint, the conformation depicted in Figure 7, shown for $(OC)_5Cr{=}C(OH)(C_6H_5)$], which is characterized by coplanarity within the carbene ligand and a staggered arrangement around the chromium−carbene bond, is found to be the most stable one for all considered chromium pentacarbonyl carbene compounds except $(OC)_5Cr{=}C(NH_2)(C_6H_5)$, where steric repulsions between the amino hydrogens and the *ortho*-hydrogens of the phenyl group impede planarity in the carbene ligand and where the amino group is oriented almost eclipsed to a *cis*-CO ligand.

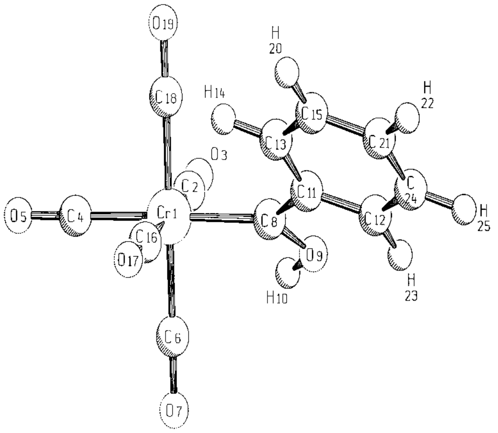

Figure 7. Optimized geometry of $(OC)_5Cr{=}C(OH)(C_6H_5)$. Important bond distances (pm) and angles (deg) are as follows: Cr1−C2, 189; Cr1−C4, 189; Cr1−C8, 205; Cr1−C18, 189; C8−C11, 148; C2−O3, 116; C4−O5, 116; C8−O9, 134; C18−O19, 116; Cr1−C8−C11, 131.8; Cr1−C8−O9, 119.4; C8−Cr1−C2, 91.4; C8−Cr1−C18, 90.7; dihedral C11−C8−Cr1−C18, 55.0; dihedral C11−C12−C24−C21, 359.3; dihedral C11−C13−C15−C21, 359.4; dihedral C13−C11−C8−O9, 169.5.

The eclipsed rotamer of Figure 7 is by only 10 kJ/mol in energy higher than the staggered one. It is already known from an early SCF study by Nakatsuji *et al.*[46] and a recent DFT study by Ziegler *et al.*[47] that the rotation around the chromium−carbene bond at heteroatom-stablized chromium carbene complexes is essentially free and that the energetic difference as well as differences in geometric parameters between an eclipsed and a staggered conformation are negligible. It has also been pointed out by Ziegler that by comparing calculated structures with experimental solid state structures[48] (Table 1) intermolecular interactions, *e.g.*, packing effects, might well compete with intramolecular interactions in determining the most stable geometric arrangement of the molecule.

Table 1 presents characteristic bond lengths of our calculated chromium complexes and compares them with experimental data. An amino instead of a hydroxy substituent at the carbene carbon atom results in a chromium−carbene bond which is longer by 5 pm for vinylcarbene complexes, reflecting the

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Table 2. Calculated CO Bond Dissociation Energies (BDE) in kJ/mol

compound	diss CO	BDE kJ/mol
$Cr(CO)_6$		198
		192[a]
$(OC)_5Cr{=}C(OH)(CH{=}CH_2)$	*cis*[b]	168[d]
	cis[c]	125[e]
	trans	202
$(OC)_5Cr{=}C(NH_2)(CH{=}CH_2)$	*cis*[b]	168
	cis[c]	115
	trans	217
$(OC)_5Cr{=}C(OH)(C_6H_5)$	*cis*[b]	154
	cis[c]	156
	trans	198
$(OC){=}Cr{=}C(NH_2)(C_6H_5)$	*cis*[b]	155
	cis[c]	154
	trans	212

[a] Ziegler's value from ref 49. [b] CO ligand which is next in space to the π-system of the carbene ligand; tetracarbonyl carbene complex as dissociation product. [c] CO ligand which is next in space to the π-system of the carbene ligand; η^3-allylidene complex as dissociation product. [d] Figure 8. [e] Figure 9.

stronger π-electron-donating character of the amino group. This donating heteroatom effect amounts to only 3 pm for phenylcarbene complexes, since the non-coplanarity within the aminophenylcarbene ligand impedes π-electron donation from the phenyl group.

CO Dissociation Processes

As outlined in the introduction, reactions of chromium carbene compounds with alkynes start by dissociation of a CO ligand. Our investigations show that the dissociation reactions

$$Cr(CO)_6 \rightarrow Cr(CO)_5 + CO \qquad (1)$$

$$(OC)_5Cr{=}C(XH)(CH{=}CH_2) \rightarrow (OC)_4Cr{=}C(XH)(CH{=}CH_2) + CO \quad \text{with } X = O, NH \qquad (2)$$

proceed without barriers, *i.e.*, they do not exhibit a transition structure. Any interaction of the metal complex with the solvent is neglected at this stage.

Since the bond dissociation energy (BDE) of a *cis*-CO ligand is lower than for a *trans*-CO ligand (Table 2), a *cis*-CO is the first to dissociate from heteroatom-stabilized chromium pentacarbonyl carbene complexes, which is in agreement with the general mechanistic proposals. With this, a *cis*-CO dissociation can lead to two structurally different dissociation products. The first one is a tetracarbonyl carbene complex (Figure 8), which is characterized by a vacant *cis*-coordination site; this complex is electron-deficient and it is implied that the vacant coordination site will be occupied by a suitable donor, be it a solvent molecule (cf. next subsection) or part of the reactant itself, *e.g.*, an acetyl group.[9] The second is an η^3-allylidene complex (Figure 9), which saturates the originally vacant ligand position site intramolecularly and is more stable than the coordinatively unsaturated tetracarbonyl carbene complex by about 43−53 kJ/mol (Table 2) for vinylcarbene, but not for phenylcarbene complexes, since the phenyl group cannot provide the necessary conformative flexibility. The η^3-allylidene complex corresponds to the CO dissociation product found by Barluenga[27] for an aminovinylcarbene complex.

The substitution of OH by NH_2 enlarges the *trans*-CO BDE by 15 kJ/mol for chromium vinylcarbene compounds, but has no significant effect on the BDE of the *cis*-CO. Moreover, the gradient of the Cr−(*cis*-CO) potential curves is the same for both the amino- and the hydroxyvinylcarbene complexes. Thus, the experimental observation that higher temperatures are needed for annulation reactions of aminophenylcarbene compared to methoxyphenylcarbene compounds cannot be explained without taking any interaction with the environment into account. Moreover, the intramolecular saturation of the vacant coordination site is more favorable for aminovinylcarbene than for (hydroxyvinyl)carbene compounds, which implies that—neglecting solvent effects—a CO might dissociate more easily from an aminovinylcarbene than from a hydroxyvinylcarbene complex.

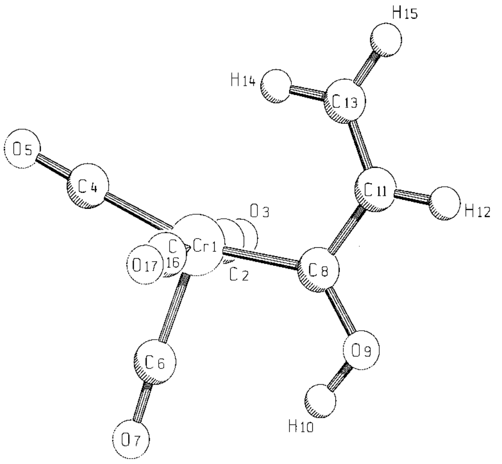

Figure 8. Optimized geometry of $(OC)_4Cr{=}C(OH)(CH{=}CH_2)$ as the first possible *cis*-CO dissociation product of $(OC)_4Cr{=}C(OH)(CH{=}CH_2)$. Important bond distances (pm) and angles (deg) are as follows: Cr1−C2, 189; Cr1−C4, 190; Cr1−C6, 180; Cr1−C8, 197; C8−C11, 147; C11−C13, 135; C2−O3, 116; C4−O5, 116; C6−O7, 117; C8−O9, 133; Cr1−C8−C11, 118.2; Cr1−C8−O9, 130.6; dihedral C11−C8−Cr1−C2, 90.9; dihedral O9−C8−C11−C13, 180.1.

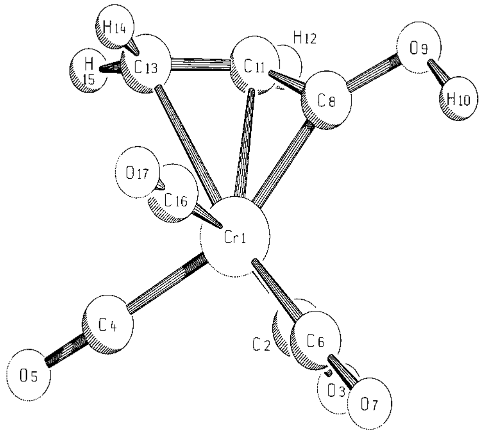

Figure 9. Optimized geometry of the η^3-allylidene complex as second possible *cis*-CO dissociation product of $(OC)_5Cr{=}C(OH)(CH{=}CH_2)$. Important bond distances (pm) and angles (deg) are as follows: Cr1−C2, 189; Cr1−C4, 190; Cr1−C6, 184; Cr1−C8, 189; Cr1−C11, 221; Cr1−C13, 237; Cr1−C16, 190; C8−C11, 144; C11−C13, 140; C2−O3, 116; C4−O5, 116; C6−O7, 117; C8−O9, 132; Cr1−C8−C11, 82.0.

There is a good agreement between our calculated CO dissociation energy for and the corresponding value of Ziegler *et al.*[49] (Table 2).

CO−Solvent Exchange Processes

The benzannulation is generally run in donating solvents like *tert*-butyl methyl ether or tetrahydrofuran (THF). Therefore, it

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(49) Li, J.; Schreckenbach, G.; Ziegler, T. *J. Am. Chem. Soc.* **1995**, *117*, 486.

Table 3. Calculated Energies (in kJ/mol) for the *cis*-CO−Water Exchange Processes

$$(OC)_5Cr{=}C(X)R + H_2O \rightarrow (OC)_4(H_2O)Cr{=}(X)R + CO$$

X	R	*cis*-CO	exchange energy[c]
OMe	vinyl	*a*	+82
		b	+98
NHMe	vinyl	*a*	+94
		b	+101
OMe	phenyl	*a*	+80
NHMe	phenyl	*a*	+97

[a] *cis*-CO next to the π-system within the carbene ligand. [b] *cis*-CO next to the heteroatom group of the carbene carbon atom. [c] The total energy of the educts is defined as energetical zero point.

is most likely that the ligand position of a dissociated *cis*-CO in a tetracarbonyl carbene complex will be occupied by a solvent molecule. In our calculations, we employed a water molecule as a model for a solvating species; in order to exclude hydrogen-bonding effects, we investigated the ligand exchange processes in detail for methoxy- and methylaminocarbene complexes.

Two points can be extracted from Table 3, which summarizes our results for the CO−water exchange processes. Firstly, the exchange of a *cis*-CO ligand, which is oriented next to the π-system within the carbene ligand is energetically more favorable than an exchange of the other *cis*-CO's. Secondly, by comparing the CO−water exchange energies of methoxy- and methylaminocarbene complexes, a significant heteroatom effect is observed. The heteroatom effect is more pronounced for the energetically favorable exchanges, where it amounts to 12−17 kJ/mol. Thus, our calculations imply that a purely σ-electron-donating solvent like THF will stabilize the vacant coordination site of a chromium tetracarbonyl methoxycarbene much more efficiently than the more electron-rich coordination site of a chromium tetracarbonyl methylaminocarbene complex.

Since all following reaction steps of the benzannulation are found to be low-barrier steps, the *cis*-CO−solvent exchange is the rate-determining step and explains the experimental observation that aminocarbene complexes react at higher temperatures than their alkoxy analogues. This is also in line with the experimental observation that a CO−P(n-Bu)$_3$ exchange in *n*-butyl ether already takes place at 50 °C for methoxyphenylcarbenes but needs more than 100 °C to occur for dimethylaminocarbene complexes.[50] However, the situation might be different if the vacant coordination site will be saturated intramolecularly (which is an alternative only for vinylcarbene complexes), as discussed in the previous subsection.

Ethyne Coordination and Ethyne−Carbene Insertion

As the next step, the coordination of ethyne and the successive ethyne−carbene insertion was studied for both possible *cis*-CO dissociation products, *i.e.*, the tetracarbonyl carbene complex (Figure 8) and the η^3-allylidene complex (Figure 9).

Ethyne Approach to a Tetracarbonylcarbenechromium. Ethyne Coordination—η^2-Ethyne−Carbene Complexes as First Intermediates. In order to investigate the ethyne coordination on tetracarbonylvinylhydroxycarbenechromium (Figure 8), we employed several reaction coordinates and found that the C_{ethyne}−$C_{carbene}$ distance is most suitable (indicated in **16**, Figure 11). Its initial value in **14** was 450 pm, assuring that the ethyne coordination proceeds unbiased. The ethyne coordination leads to the formation of two minima: a rotamer of an η^2-ethyne−carbene complex **15**, in which the C_{ethyne}−C_{ethyne} bond is oriented perpendicular to the chromium−carbene bond, and a rotamer **16**, in which the C_{ethyne}−C_{ethyne} bond is oriented parallel to the chromium−carbene bond. Both rotamers are energetically equal within 2 kJ/mol. The distance of chromium to the carbon atoms of ethyne, 224 pm (parallel isomer), a C_{ethyne}−C_{ethyne} distance of 126 pm, and an H_{ethyne}−C_{ethyne}−C_{ethyne} bond angle of 155° indicate an intermediate η^2-coordination. The experimental findings for the *ortho*-alkynylarylcarbene complexes of chromium **B**[25] and tungsten **C**[24] (Figure 10) (values for the tungsten complex are in parentheses) are 235 (237) pm (metal−C_1), 242 (240) pm (metal−C_2), 123 (122) pm (C_1−C_2), 171° (169°) (C_{aryl}−C_1−C_2 bond), and 157° (152°) (C_1−C_2−Si(C_{phenyl})), respectively. We note that a stronger η^2-coordination in these complexes might be hindered by the rigid C_2 arene bridge that connects the carbene and alkyne group as well as by the sterically demanding terminal alkyne substituent, at least this is indicated by the unsymmetric η^2-coordination.

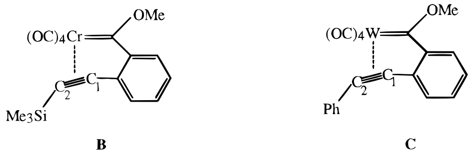

Figure 10. Examples of experimentally isolated *o*-alkynylarylcarbene complexes.[24,25]

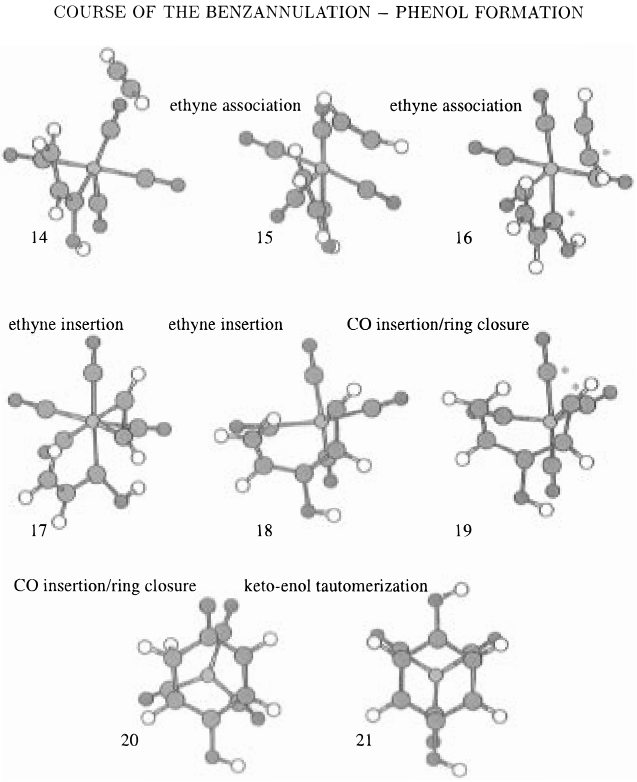

Figure 11. **14** $(OC)_4Cr{=}C(OH)(CH{=}CH_2)$ + approaching ethyne; **15** minimum, rotamer of an η^2-ethyne−carbene complex, **not relevant** for the benzannulation; **16** minimum, rotamer of an η^2-ethyne−carbene complex, **relevant** for the benzannulation; **17** transition structure of the ethyne−carbene insertion; **18** minimum, η^3-vinylallylidene complex; **19** transition structure of the CO insertion + simultaneous ring closure; **20** minimum, η^4-cyclohexadienone complex; **21** minimum, η^6-hydroquinone complex. The asterisks (*) indicate the atoms defining the reaction coordinate.

Ethyne Insertion—η^3-Vinyl- or η^3-Phenylallylidene Complexes as Second Intermediates. Only the η^2-ethyne−carbene

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(50) Unpublished results.

(51) Bauta, W. E.; Wulff, W. D.; Pavkovic, S. F.; Zaluzec, E. J. *J. Org. Chem.* **1989**, *54*, 3249.

(52) Jost, A.; Rees, B.; Yelon, W. B. *Acta Crystallogr. B* **1975**, *B31*, 2649.

(53) Rees, B.; Mitschler, A. *J. Am. Chem. Soc.* **1976**, *98*, 7918.

Table 4. Calculated Energies[a] (in kJ/mol) of the Ethyne−Carbene Insertion, Starting from a Solvent-Stabilized Tetracarbonyl Carbene Intermediate, Forming an η^3-Vinyl- or η^3-Phenylallylidene Complex via an η^2-Ethyne−Carbene Complex

$(OC)_4(H_2O)Cr{=}C(X)R$[b]			η^2-ethyne− carbene	transition structure	η^3-allylidene[c]
X	R				
		BP86, Optimized Geometries			
OH	vinyl	0	+13	+27	−77
		0[d]	−26	−12	−116
NH_2	vinyl	0	+13	+43	−65
		0[d]	−12	+18	−90
OH	phenyl	0	+12	+24	−81
NH_2	phenyl	0	−4	+24	−81
		B3LYP, BP86 Geometries			
OH	vinyl	0	+33	+57	−50
NH_2	vinyl	0	+34	+75	−36

[a] Energy of a free ethyne, respectively, a free water is included. [b] Defined as energetical zero point. [c] Either η^3-vinylallylidene or η^3-phenylallylidene complex intermediates. [d] Starting from an intramolecularly stabilized η^3-allylidene complex.

complex **16** is relevant for the subsequent ethyne−carbene insertion step and thus acts as the first intermediate of the benzannulation. It is endothermic by 13 kJ/mol compared to the water-stabilized tetracarbonyl carbene complex, if the energies of a free ethyne molecule and a free water molecule are taken into account (Table 4). In the case of an aminophenylcarbene complex, the exchange of a water molecule by an ethyne molecule is even marginally exothermic. This is not surprising: On one hand, a water stabilization of a tetracarbonyl aminocarbene complex is less efficient than the stabilization of its hydroxycarbene analogue (Table 3); on the other hand, the ethyne molecule provides some π-accepting character, which stabilizes especially the more electron-rich aminocarbenes. Compared to their pentacarbonyl educts, the η^2-ethyne−carbene complex intermediates are almost endothermic to the same amount (about 100 kJ/mol) for all investigated carbene complexes (see Table 7).

From its originally parallel η^2-coordinated position **16**, ethyne moves right above the chromium−carbene bond, still staying almost in plane with the chromium−carbene bond. At the corresponding transition structure **17**, all three carbon atoms participating in this step are coordinated to the chromium center. The corresponding chromium−carbon distances are between 200 and 220 pm. Due to these energetically very favorable η^3-interactions, it requires an activation energy of only 14 kJ/mol (Table 4) to get from the first intermediate **16** to the alkyne insertion product, an η^3-vinylallylidene complex **18** (this is not to be confused with the η^3-allylidene complex as product of the *cis*-CO dissociation). Since a new carbon−carbon bond is formed and a former ethyne carbon atom now acts as a carbene carbon atom, the η^3-vinylallylidene complex **18** is more stable by 90 kJ/mol than the preceding intermediate **16** (Table 4). The low-energy barrier hampers the isolation of an η^2-ethyne−carbene intermediate **16** during a benzannulation.

The regioselectivity observed for the benzannulation using unsymmetric alkynes can be explained in a sense that, in order to minimize steric congestion during the alkyne−carbene coupling, the sterically less shielded alkyne carbon atom prefers to be added to the carbene carbon atom in the η^2-ethyne−carbene complex of type **16**.

The energetics of the ethyne−carbene insertion are significantly affected by the nature of the heteroatom (Table 4). The insertion requires an additional 16 kJ/mol of activation energy for aminocarbene compared to hydroxycarbene complexes, since the pronounced π-donating character of the amino group reduces the π-electron density at the chromium−carbene bond. From Table 4 it is also observed that, starting from an intramolecularly stablized tetracarbonyl complex (an η^3-allylidene complex), the ethyne−carbene insertion requires only a small amount of activation energy. This is in agreement with the experimental findings of Barluenga, who carried out such a reaction at −25 °C with a morpholino educt.[27]

At this point, we should make a general comment on the calculated energy barriers. Firstly, our calculated SVP barriers are smaller than the SV barriers (the SV barriers are supplied with the supporting information), as can be expected. Secondly, it is well-known that pure DFT methods underestimate barriers, the local density approximation much more than the gradient-corrected functionals. The B3LYP barriers are known to be larger, since a certain percentage of the Hartree-Fock exchange is incorporated into the functional. Our calculated B3LYP barriers are always larger than the BP86 ones (10−15 kJ/mol), but might still be too small. The difference in barriers between amino and hydroxy compounds, however, is affected by neither the functional nor the basis set.

Ethyne Approach to an η^3-Allylidene Complex. Again we tested several reaction coordinates and found that the one indicated above is most suitable here. However, in none of the considered cases any kind of an η^2-ethyne complex could be formed, simply because there is no vacant coordination site available in an η^3-allylidene complex (Figure 9). The consequence would be a highly energetic attack of the ethyne at the carbene carbon atom (the energetics of such an attack are supplied with the supporting information). Therefore, the η^3-allylidene complex as a direct product of the *cis*-CO dissociation will give up its intramolecular η^3-bonding in order to become accessible for an ethyne insertion. Such a process is reversible, as shown by Barluenga;[27] the exposed coordination site can then be occupied by a solvent, a CO, or an ethyne molecule.

CO Insertion and Ring Closure to η^4-Cyclohexadienone Complex Intermediates

At this point, we have determined that a *cis*-CO−ethyne exchange, leading to a high-energy η^2-ethyne−carbene complex intermediate **16** or **23** (Figures 11 and 12), will be followed by an ethyne−carbene insertion, resulting in the formation of η^3-vinyl- (**18**) or η^3-phenylallylidene (**25**) intermediates. The next step should be an intramolecular coupling of the carbene carbon atom (a former ethyne carbon atom) with a carbon monoxide ligand. In the following, we discuss the further reactions of η^3-vinyl- and η^3-phenylallylidene complex intermediates separately.

Benzannulation of Vinylcarbenes−η^4-Cyclohexadienone Complexes as Final Intermediates. Starting from the η^3-vinylallylidene intermediate **18** (Figure 11), we employed the distance between the carbene carbon atom (former ethyne carbon atom) and the carbon atom of the most suitable CO ligand as reaction coordinate for the CO insertion step (indicated in **19**). The CO ligand was found to move toward the vinylallylidene ligand and thus acquires a favorable position for the subsequent CO insertion. We calculate an activation energy of only 22 kJ/mol for this step (Table 5); chromium softens all bond reorganization processes energetically by keeping all relevant carbon atoms coordinated, nicely demonstrated by the distances of chromium to CO and the carbene carbon atom at the transition structure **19**, 184 and 190 pm. Consequently, no electron deficiencies will arise, neither at chromium nor at the carbon atoms. Due to the small energy barrier, the isolation of the preceding η^3-vinylallylidene intermediate **18** at the benzannulation will be difficult.

With the CO insertion a ring closure takes place, connecting the CO carbon atom and the terminal carbon atom of the

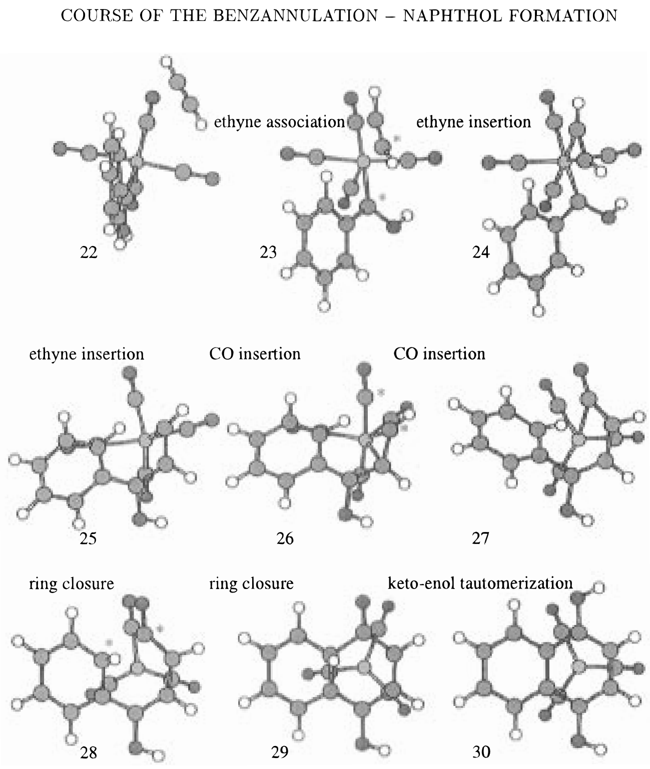

Figure 12. **22** $(OC)_4Cr{=}C(OH)(C_6H_5)$ + approaching ethyne; **23** minimum, η^2-ethyne−carbene complex; **24** transition structure of the ethyne−carbene insertion; **25** minimum, η^3-phenylallylidene complex; **26** transition structure of the CO insertion; **27** minimum, η^4-vinylketene complex; **28** transition structure of the ring closure; **29** minimum, η^4-benzocyclohexadienone complex; **30** minimum, η^6-4-hydroxynaphthol complex The asterisks (*) indicate the atoms defining the reaction coordinate.

Table 5. Calculated Energetics (in kJ/mol) of the CO Insertion Step, Starting from η^3-Vinylallylidene Complex Intermediates

	η^3-vinyl-allylidene[a]	transition structure	η^4-cyclo-hexadienone
	BP86, Optimized Geometries		
OH	0	+22	−194
NH_2	0	+30	−198
	B3LYP, BP86 Geometries		
OH	0	+34	−193
NH_2	0	+42	−192

[a] Defined as energetical zero point.

vinylallylidene ligand to form an η^4-cyclohexadienone intermediate **20**. It is lower in energy by 194 kJ/mol (Table 5) than the preceding η^3-vinylallylidene intermediate **18** since two new carbon−carbon bonds are formed.

In variation with all previous mechanistic proposals, which were generally formulated for carbene complexes with an α,β-double bond as part of an aromatic ring, we found no η^4-vinylketene complex intermediate. We also employed a ring opening coordinate at the η^4-cyclohexadienone complex in order to check for the existence of such an intermediate, but we did not find any appropiate local minimum.

The CO insertion will only be affected to a small extent by the nature of the heteroatom (8 kJ/mol) (Table 5), which was not expected from the general mechanistic proposals.

Table 6. Calculated Energetics (in kJ/mol) of the CO Insertion and the Successive Ring Closure Step, Starting from η^3-Phenylallyidene Complex Intermediates (IM)

	IM[a]	transition structure	IM
		CO Insertion	
η^3-phenylallyidene			η^4-vinylketene
OH	0	+22	−50
NH_2	0	+28	−47
		Ring Closure	
η^4-vinylkene			η^4-benzocyclohexadienone
OH	0	+23	+10
NH_2	0	+30	+14

[a] Defined as energetical zero point.

Benzannulation of Phenylcarbenes—η^4-Vinylketene Complexes as Third and η^4-Benzocyclohexadienone Complexes as Final Intermediates. CO Insertion in η^3-Phenylallylidene Complexes—η^4-Vinylketene Complex Intermediates. Starting from the η^3-phenylhydroxyallylidene intermediate **25** (Figure 12), we employed the same reaction coordinate (indicated by asterisks in **26**) for the CO insertion step as in the case of the vinylcarbene complexes. The CO ligand was found to move toward the phenylallylidene ligand and obtains a favorable position for the forthcoming CO insertion. At the transition structure **26**, the carbene carbon atom and the inserting CO are strongly coordinated to the metal center; the corresponding distances are 184 and 191 pm, and neither at chromium nor at the carbon atoms electron deficiencies arise. Due to the pronounced template character, the energy barrier is as small as 22 kJ/mol (Table 6). This makes it difficult to isolate the preceding η^3-phenylallylidene intermediate **25** in this instance of the benzannulation reaction.

The carbon atom in **26** which will be connected to the CO carbon atom is part of a phenyl ring. It is, in contrast to its vinylallylidene analogue neither electronically and/or coordinatively unsaturated, nor can it rehybridize easily. Therefore, an η^4-vinylketene intermediate **27** will be formed, which is lower in energy by only 50 kJ/mol (Table 6) compared to the preceding intermediate **25**, since only one new carbon−carbon bond has been formed. The nature of the heteroatom has again only a small influence on the activation energy, the difference of the corresponding barriers amounting to 6 kJ/mol (Table 6).

The calculated ketene bond lengths—143 pm for the ketene carbon−carbon bond and 120 pm for the carbon−oxygen bond—and the ketene bond angle of 143 degrees are typical for η^4-vinylketene complexes.[28]

Ring Closure from η^4-Vinylketene Complex to η^4-Benzocyclohexadienone Complex Intermediates. The next step of the benzannulation is straightforward: a ring closure from the η^4-vinylketene intermediate **27** to an η^4-cyclohexadienone intermediate **29** (the reaction coordinate is indicated in **28**). Although a new carbon−carbon bond is formed, this step is endothermic by 10 kJ/mol (Table 6), because the planarity and therefore the aromaticity of the phenyl ring is strongly perturbed in the product. Nevertheless, the calculated activation energy is small, 24 kJ/mol, caused by the pronounced template character of this reaction step. The nature of the heteroatom affects the energetics of this reaction step only to a small amount, 7 kJ/mol (Table 6).

From Educts to Aromatic Products—An Energetic Overview

In the former sections we investigated the mechanism of the benzannulation of heteroatom-stabilized pentacarbonyl carbene complexes with ethyne, resulting in the formation of η^4-cyclohexadienone intermediates **20** and **29**. Finally, we present an energetic overview from educts to aromatic products **21** and **30** (Table 7). The total energy of the educts (chromium

Table 7. Calculated Relative Energies (in kJ/mol) of Educts,[a] All Intermediates,[b] (IM) and Products[b] of the Benzannulation[j]

$(OC)_5Cr{=}C(X)R$ X	R	TC[c] solv	1st IM[d]	2nd IM[e]	3rd IM[f]	4th IM[g]	product[h]
			BP86, Optimized Geometries				
OH	vinyl	0	+86	+99	+9		−185[i]	−266
NH_2	vinyl	0	+90	+103	+25		−173[i]	−246
OH	phenyl	0	+84	+96	+3	−47	−37	−211
NH_2	phenyl	0	+104	+100	+23	−24	−10	−185
			B3LYP, BP86 Geometries				
OH	vinyl	0	+65	+98	+15		−178[i]	−249
NH_2	vinyl	0	+68	+102	+32		−160[i]	−228

[a] Energy of a free ethyne is included. [b] Energy of a free CO (water) is included. [c] $(OC)_4(H_2O)Cr{=}C(X)R$ (solvated tetracarbonyl carbene). [d] η^2-Ethyne-carbene. [e] η^3-Allylidene. [f] η^4-Vinylketene. [g] η^4-Cyclohexadienone. [h] η^6-Phenol or η^6-naphthol. [i] 3rd IM at the phenol formation. [j] The total energy of the educts is defined as energetical zero point.

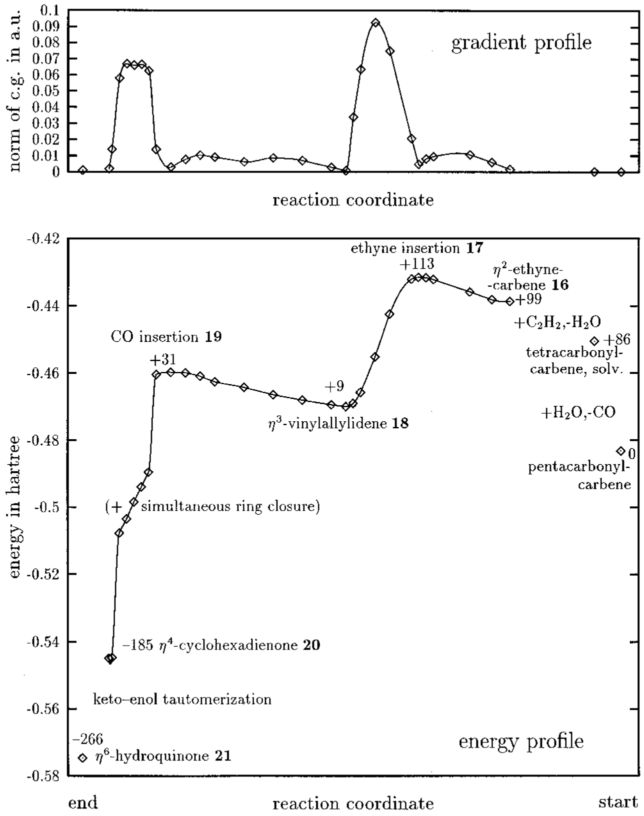

Figure 13. Gradient and energy profile for the phenol formation. The relative energies are given in kJ/mol (SVP basis, BP86 functional). The boldfaced numbers refer to the structures shown in Figure 11.

pentacarbonyl carbenes plus a free ethyne) is defined as the energetical zero point, and the energy of a free carbon monoxide molecule is added to the energies of all subsequent structures.

The keto−enol tautomerization from η^4-cyclohexadienone complex intermediates to aromatic products is accompanied with a considerable gain in energy (Table 7): about 80 kJ/mol for the vinylcarbenes, where a phenol system is formed by the tautomerization step, and about 175 kJ/mol for the phenylcarbenes, where a naphthol system is produced. The total benzannulation is significantly more exothermic for vinylcarbenes than for phenylcarbenes (about 55−60 kJ/mol), since in the former case a new aromatic phenol system is created, whereas in the latter case only an existing phenol system is augmented to an aromatic naphthol system.

The energy and gradient profiles are shown for the hydroxycarbenes in Figures 13 and 14.

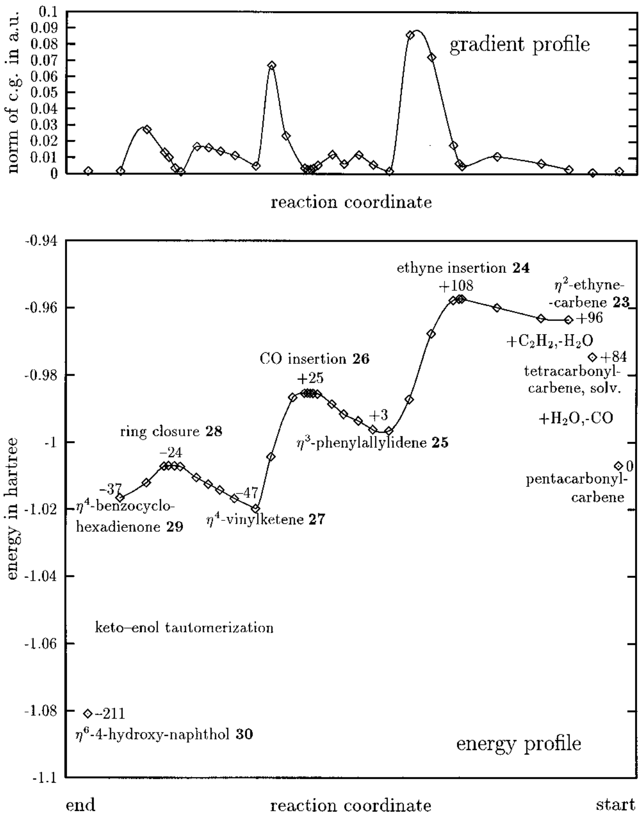

Figure 14. Gradient and energy profile for the naphthol formation. The relative energies are given in kJ/mol (SVP basis, BP86 functional). The boldfaced numbers refer to the structures shown in Figure 12.

Conclusion

We presented a density functional investigation of the benzannulation reaction of heteroatom-stabilized chromium carbene complexes with ethyne. Independent of the detailed mechanism, the benzannulation is strongly exothermic for hydroxy- and amino-substituted phenyl- and vinylcarbene complexes. It is found to be more exothermic for hydroxycarbenes than for aminocarbenes and much more exothermic for vinylcarbenes than for phenylcarbenes, since in the former case a new aromatic system is created.

We find that the rate-determining step is the dissociation of a *cis*-CO ligand. The vacant coordination site may be saturated either intramolecularly, forming η^3-allylidene complexes (this is an alternative only for vinylcarbenes), or intermolecularly by a solvent. The tetracarbonyl hydroxycarbene complexes are stabilized significantly stronger by a purely σ-donating solvent than their amino analogues, which explains the experimental observation that aminocarbenes react at higher temperatures than their hydroxy analogues.

The next reaction steps are an ethyne coordination, forming η^2-ethyne−carbene complex intermediates, and an ethyne insertion into the chromium−carbene bond, producing η^3-allylidene complex intermediates. Already at the ethyne−carbene coupling step the regioselectivity of the benzannulation is determined.

A CO insertion follows. In the case of phenylcarbene complex educts, η^4-vinylketene complex intermediates are formed, which react by a ring closure to η^4-benzocyclohexadienone complexes, whereas in reactions of vinylcarbenes, η^4-cyclohexadienone complexes are produced without any further barrier of activation. η^4-Vinylketene complexes are the most stable, however only weakly exothermic, intermediates in the naphthol formation, and η^4-cyclohexadienone complexes are the most stable and strongly exothermic intermediates in the phenol formation. This has remarkable experimental consequences: vinylcarbene complexes should generally produce six-membered rings, whereas a formation of six-membered rings should rarely be observed for *ortho*-disubstituted phenylcarbene chromium complexes.

All reaction steps, except the rate-determining *cis*-CO dissociation, are (*i*) characterized throughout by low-energy barriers due to the pronounced template character of the reaction and (*ii*) only to a small extent affected by the nature of the heteroatom. As a result, an experimental observation of intermediates of the benzannulation reaction is difficult and the fact that for aminocarbene complexes cyclopentannulation usually prevails over benzannulation should not exclusively be determined by the energetics of the CO insertion step.

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Supporting Information Available: Cartesian coordinates of all optimized (BP86 functional, SVP basis) educts, intermediates, transition structures, and products; the energetics calculated with the SV basis set; and the energetics of the ethyne association on both possible *cis*-CO dissociation products (27 pages). See any current masthead page for ordering and Internet access instructions.

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